Discontinuous Electrophoresis Deposition for Dye-Sensitized Solar Cells

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***Abstract*—As one method of making dye sensitized solar cell (DSSC), electrophoresis deposition (EPD) which laminates TiO_2 on anode using two electrodes is practical way. Because it linked with low-temperature firing in case of espousing plastic substrate. In addition to being able to cut cost of experimental devices. However it has been reported that cracks appear and get bigger on surface of TiO_2 layer depending TiO_2 thickness. In this paper, we conducted discontinuous electrophoresis and compared with continuous about surface condition of TiO_2 layer and conversion efficiency. We used a glass substrate coated FTO as an anode and pt-FTO as a cathode. We adopted MK-2 dye which was an organic pigment. As a result of experiment, we could realize improvement of TiO_2 surface condition and progress conversion efficiency in case of discontinuous (2.47%) than continuous (2.08%) under illumination with 100 mWcm^{-2} (AM 1.5) simulated sunlight. Moreover, we proved that it was better dividing number of times.**

***Index Terms*—DSSC, TiO_2 layer, Electrophoresis deposition, discontinuous, Mk-2 dye, drying**

I. Introduction

In many countries, economy and people's lives greatly depend on fossil energy like petroleum, coal and natural gas. But it is said that fossil energy will run out several decades after so it is finite resources. When we take into account increasing world population mainly in developing countries, it is worried that consumption of fossil energy increases and its depletion accelerates further. Also it can be thought of possibility that progressing global warming with increasing suddenly carbon dioxide by consumption of fossil energy leads to another problems which are abnormal whether, scarcity of food and rise in sea level and so on. Because of these problems, regenerated energy which is low impact to environment is receiving a lot of attention. Among them solar cell that converts light energy into electrical energy is effective choices.

There are some type of solar cells, and it can sort to three patterns as silicon, compound and organic system. The streamline solar cells are crystalline silicon solar cells and multicrystal silicon solar cells nowadays. These conversion efficiency are high but the two cost are high too in addition compound system. On the other hand organic solar cells have low conversion efficiency, but their costs are low. DSSC developed by Gratzel in 1991 has an epoch-making structure. It has been researched all over the world in recent years.

The feature of DSSC is low cost, flexible, and environmental load so that it has simpler structure than existing silicon solar cells. Its operating principle is very different compared with other solar cells, and generates electricity by absorbing the light. It is generally used ruthenium complex as the dye to absorb more wide rage light. However it is worried that ruthenium is a high price and little deposits because of a rare metal. It has ill effects on the human body to have toxicity furthermore. These are in consistent with merits of DSSC.

The pigment is generally used to adsorb in TiO_2 which is laminated on anode. There are some laminating ways doctor-blade, spin-coating and electrophoresis deposition method. The EPD method is to be suited to mass production of cells. It has reported that the cell performance get worse as well as getting bigger cracks of TiO_2 layer if phoresis time gets longer or increasing amount of TiO_2 [1]-[4].

In our experiment, we proposed discontinuous electrophoresis deposition method to decrease cracks on TiO_2 layer. We carried out surface observation and measured conversion efficiency comparing continuous phoresis time and discontinuous which was divided at regular intervals. As stated above demerit considered, we used organic pigment, MK-2 dye.

II. Theory

A. *Dye-Sensitized Solar Cell*

Dye-sensitized solar cell is organic solar cell consisted of anode, TiO_2, pigment, electrode and cathode as shown in Fig. 1. Though silicon solar cell takes high power generation cost as manufacturing process is complicated, DSSC can cut down expense as having simple structure. In 2013, Gratzel team announced the highest conversion efficiency of 15% [5].

Power generation principle is rather different from pn junction of silicon solar cells. First of all, when the light irradiates pigments which are adsorbed in TiO_2 layer, electrons emit from pigments and pigments are oxidized. Electrons go through TiO_2 layer and external circuit. They reached from external circuit to counter electrode are repeated oxidation-reduction reaction on the interface

Manuscript received July 12, 2015; revised September 11, 2015.

doi: 10.18178/ijpmbs.4.4.218-222

between counter electrode and electrolytic solution. The same reaction happens between electrolytic solution and pigments too. Pigments are deoxidized and back to the original state. These reactions follow by successive as long as the light is irradiated to pigments.

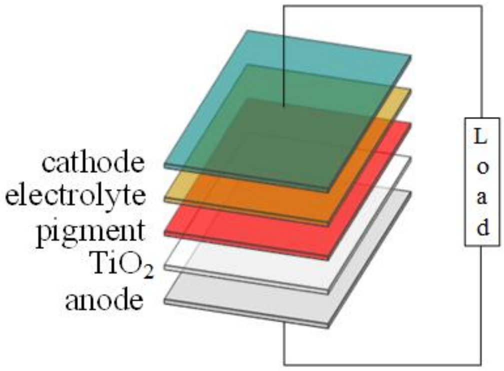


Figure 1. A fundamental structure of DSSC.

B. *Electrophoresis Deposition (EPD)*

EPD is the way to laminate materials on substrate to utilize electrophoresis phenomenon [6]-[8] shown in Fig. 2. When particles are scattered in solution, they are taken a charge positive or negative by various factors. When electrodes are inserted into this solution and applied direct current (DC), particles move to opposite electrode toward their charge. This is electrophoresis phenomenon. There are some advantages to EPD. The formation of film is comparatively early and control is easy. It doesn't depend on the size of electrode and be able to use not a plane one. By contrast, the forms of materials are limited by membranous and conductive substrates are needed.

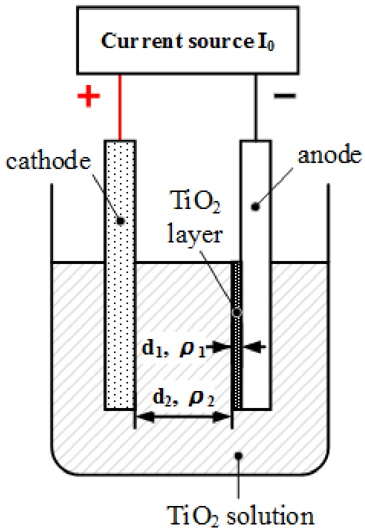


Figure 2. A theory figure of EPD.

$$V_0(t) = \frac{\rho_1}{S_0} d_1(t)\, I_0 + \frac{\rho_2}{S_0} d_2(t)\, I_0 \quad (1)$$

$$V_0(0) = d_2 E \quad (2)$$

The potential difference during electrophoresis is by the following equation [9]. V_0 is the potential difference between anode and cathode. S_0 is the area of two electrodes, d_1 is the TiO_2 layer thickness the side of anode, d_2 is the distance from the surface of TiO_2 layer to cathode, ρ_1 is the resistivity of TiO_2 layer, ρ_2 is the resistivity of TiO_2 solution, t is electrophoresis time, I_0 is direct current (DC) from electric current source. E is an electric field.

III. Experimental Procedures

At first, we used 0.5g of TiO_2 powder (P25, particle) and 100mL ethanol (wako, 95.1%) to make TiO_2 solution. They were mixed into container with stirrer and stirred with the speed of 700rpm at 25℃ for 60min by magnetic stirrer.

Then, in the electrophoresis deposition procedure [10]-[12], anode (FTO-glass, 20×20×1.8mm) was sterilized cleaning with ethanol diluted with water (8:2). Another electrode, cathode (Aluminum, 20×20×1mm) and anode were fixed parallel, leaving a distance of 1cm with silicon. They were immersed in TiO_2 solution, and the current was constant at 0.12mA from current source (ADVANTEST, R6144). The temperature of electrophoresis deposition (EPD) was set at 25℃, electrophoresis time at 100sec for TiO_2 layer. The FTO-glass with TiO_2 layer underwent sintering at 450℃ (5℃/min) for 60min [13], [14] into electric furnace (AS ONE, SMF-1). In case of discontinuous electrophoresis deposition (50sec×2), we conducted EPD for 50sec first.

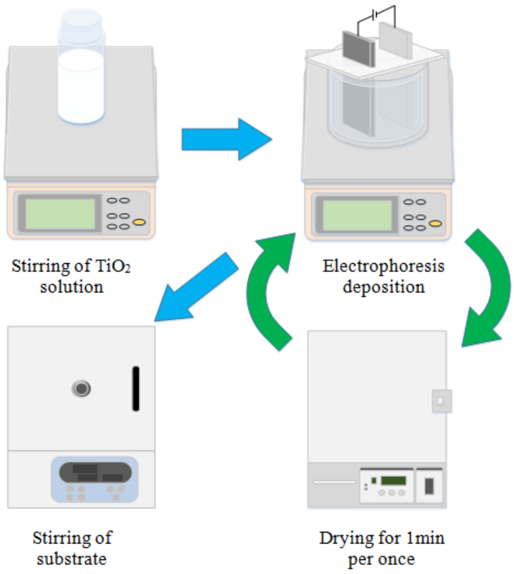


Figure 3. Discontinuous electrophoresis deposition procedure.

Next, two substrates with silicon were taken out from TiO_2 solution and dried at 40℃ for 1min into a drier (iuchi, DO-450). We conducted EPD for 50sec a second time. When we conduct discontinuous electrophoresis deposition (25sec×4), we conducted four times of EPD for 25sec and drying three times as shown in Fig. 3. After the drying, substrate was adsorbed pigment, MK-2 dye at 25℃ for 3hours. It was dried at 80℃ for 5min adsorbing later. This pigment solution was consisted of 10mg Mk-2 dye and 108mL toluene. The electrolyte was blended at 25℃ [15]. 0.1M LiI, 0.6M 1, 2-dimethyl-3-propylimidazolium iodide, 0.2M I_2, 0.5M 4-tertbutylpridine, 10mL acetonitrile were mixed. The mending tape (Scotch Brand tape, 0.058mm thickness) were used as spacer like Fig. 4. This tape cut 0.25cm^2 square was stuck on TiO_2 layer with MK-2 dye. We dropped electrolyte on this square and sealed by cathode (pt-FTO).

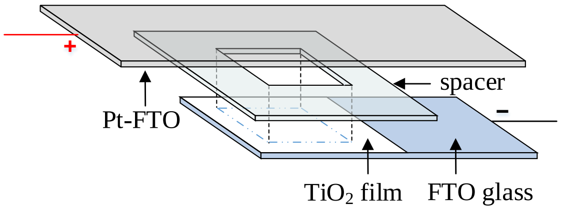


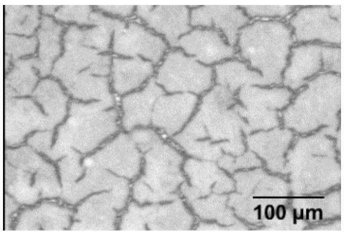
Figure 4. DSSC made by this experiment.

After made of DSSC shown in Fig. 4, conversion efficiency was obtained with solar simulator (OAI, TriSOL) by simulating the Sunlight (AM 1.5, 100mWcm^{-2}). The surface images of TiO_2 layer were got by metallurgical microscope (OLYMPUS BX60M). TiO_2 thicknesses were obtained by step gauge (BRUKER DektakXT).

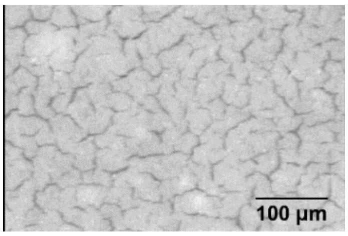
IV. Results and Discussion

A. *EPD Evaluation of the Surface of TiO_2 Layer*

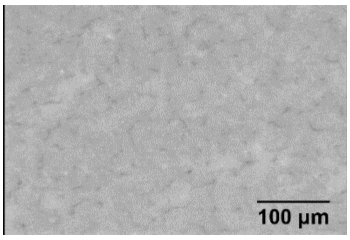
Fig. 5 shows the microscope images which are surface of TiO2 layer. All of images are by both eyepiece and objective lens with a magnifying power of 10. Fig. 5 (a) was continuous EPD for 100sec. A lot of cracks appear in the surface of TiO_2 layer. It is estimated that it is better for cell performance not to exist these cracks. Because pigment can't adsorb in these part of cracks.



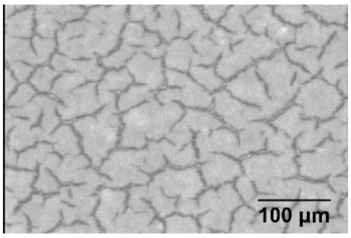
(a) Continuous EPD for 100sec



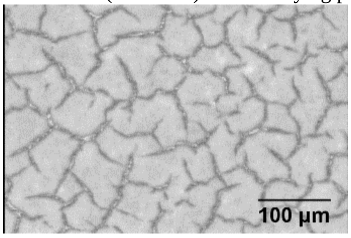
(b) Discontinuous EPD (50sec×2) with drying procedure



(c) Discontinuous EPD (25sec×4) with drying procedure



(d) Discontinuous EPD (50sec×2) without drying procedure



(e) Discontinuous EPD (25sec×4) without drying procedure

Figure 5. Microscope images continuous and discontinuous EPD.

Fig. 5 (b) shows discontinuous EPD (50sec×2). Compared with Fig. 5 (a) and (b), cracks of figure (b) are reduced from TiO2 layer than figure (a). From this result, discontinuous EPD is effective than continuous EPD. Fig. 5 (c) shows discontinuous EPD (25sec×4). This pattern is able to say the best way so that cracks are reduced still more than other patterns. In other words, multiplying the number of times that EPD is conducted is well. Fig. 5 (d) and (e) are discontinuous EPD (50sec×2) without drying procedure. We found that this images are much the same as each other. They are worse than discontinuous EPD with drying procedure, although they are better than continuous EPD. This result implies that drying procedure is essential in discontinuous EPD.

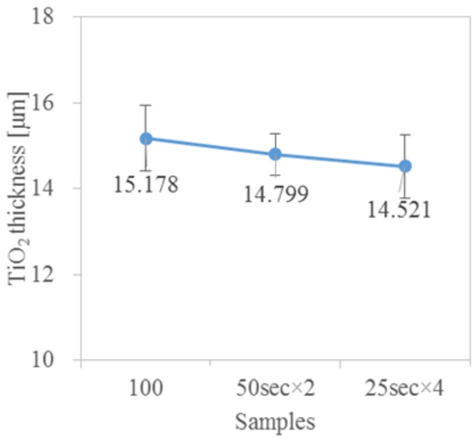


Figure 6. TiO_2 thickness per samples.

Fig. 6 is a graph about average of TiO_2 thickness. The standard deviations are shown in graph. The longer EPD time is, the thinner TiO_2 thickness slightly is, though samples of TiO_2 thickness are stable around 15μm. It was supposed TiO_2 particles were deposited in the bottom as it takes long time in discontinuous EPD procedure than continuous.

B. *Cell Efficiency Measurement*

Table I shows the highest short circuit current densities, open circuit voltages, fill factor, and conversion efficiencies for DSSC made from TiO_2 powder of different thickness with MK-2 dye with spacer area of 0.25 cm^2 under illumination with 100mWcm^{-2} AM1.5 simulated sunlight. The TiO_2 layer made for 100sec by continuous EPD shows short circuit current density of 9.12 mAcm^{-2}, open circuit voltage of 693 mV and an energy conversion efficiency of 2.24%. Discontinuous EPD (50sec×2) shows current density of 9.93 mAcm^{-2}, circuit voltage of 699 mV and conversion efficiency of 2.32%. In case of discontinuous EPD (25sec×4), current density is 10.13 mAcm^{-2}, circuit voltage of 694 mV and conversion efficiency of 2.51%. The three patterns procedure is nearly the same fill factor. From Table I result, the higher current density is, the higher conversion efficiency becomes in this experiment. The conversion efficiency of sample (50sec×2) is lower than sample (25sec×4) regardless of having higher circuit voltage. It is believed that lower current density is cause.

TABLE I: PROPERTIES OF DSSC BY DIFFERENT THICKNESS

Samples	100	50×2	25×4
Current (Jsc, mA/cm^2	9.12	9.93	10.13
Voltage (Voc, mV)	693	699	694
Fill Factor	0.35	0.34	0.35
Efficiency (%)	2.24	2.32	2.51

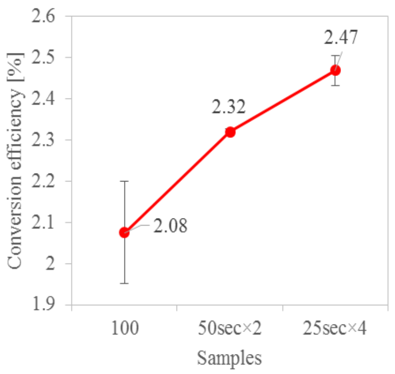


Figure 7. The average of conversion efficiency per samples.

Fig. 7 shows the relationship between EPD time by different procedure and conversion efficiency. The standard deviations are shown in graph as same as Fig. 6. The variability of samples (50sec×2) is very small compared to other samples because the variability of TiO_2 thickness are small too. The difference in conversion efficiency of 100sec samples is large in Fig. 7 though unevenness of TiO_2 thickness is never large than samples (25sec×4) in Fig. 6. This is the cause of not only variability of TiO_2 thickness but also size of cracks. If this size is large, a lot of pigments aren't adsorbed in TiO_2 layer. Quantity of MK-2 dye is also different per substrates because of difference of TiO_2 thickness and cracks. It is considered that these factors influence this result.

V. CONCLUSION

In this study, we proposed improvement of the surface of TiO_2 layer by discontinuous EPD method and evaluated cell performances using MK-2 dye.

From these results of experiment, the best way of discontinuous EPD for TiO_2 layer of electrode was four times of EPD for 25sec, three times of drying substrate at 40℃ for 1min. Drying procedure is very important for TiO_2 layer.

The DSSC prepared by this method could achieve current density of 10.13 mAcm^{-2}, circuit voltage of 694mV, 0.35 fill factor and the highest conversion efficiency of 2.51%.

ACKNOWLEDGEMENT

The authors wish to thank to Minemoto laboratory in Ritsumeikan university. We got to use Solar simulator (OAI, TriSOL) and Step gauge (BRUKER DektakXT) for simulating DSSC performance.

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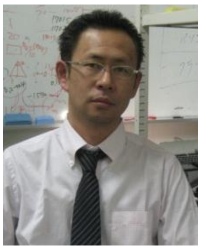

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